

Frequency Dependent Specific Heat of Amorphous Silica: A Molecular Dynamics Computer Simulation

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Abstract. We use molecular dynamics computer simulations to calculate the frequency dependence of the specific heat of a SiO_2 melt. The ions interact with the BKS potential and the simulations are done in the NVE ensemble. We find that the frequency dependence of the specific heat shows qualitatively the same behavior as the one of structural quantities, in that at high frequencies a microscopic peak is observed and at low frequencies an α -peak, the location of which quickly moves to lower frequencies when the temperature is decreased.

INTRODUCTION

The dynamics of supercooled liquids can be studied by many different techniques, such as light and neutron scattering, dielectric measurements, NMR, or frequency dependent specific heat measurements, to name a few [1]. In order to arrive at a better understanding of these systems also various types of computer simulations have been used to supplement the experimental data. However, essentially all of these simulations have focussed on the investigation of *static* properties or have studied the time dependence of *structural* quantities, like the mean squared displacement of a tagged particle or the decay of the intermediate scattering function. What these simulations have not addressed so far, apart from a noticeable study of Grest and Nagel [2], is the time dependence of thermodynamic quantities, like the specific heat. The reason for the lack of simulations in this direction is that the accurate determination of this quantity in a simulation is very demanding in computer resources because of its collective nature. This fact is of course very regrettable since one of the simplest ways to determine the glass transition temperature in a real experiment is to measure the (static) specific heat. Using ac techniques it is today also possible to measure the *frequency dependent* specific heat, $c(\nu)$, and thus to gain more insight into this observable [3]. What is so far not possible in real experiments is to measure $c(\nu)$ at frequencies higher than 1MHz, and thus the influence of the microscopic dynamics, which is in the THz range,

cannot be investigated. For computer simulations it is, however, no problem to study $c(\nu)$ also at these high frequencies and in this paper we report the outcome of such an investigation for the strong glass former silica.

MODEL AND DETAILS OF THE SIMULATION

The silica model we use is the one proposed by van Beest *et al.* [4]. In this model the interaction $\phi(r_{ij})$ between two particles i and j a distance r_{ij} apart is given by a two body potential of the form

$$\phi(r_{ij}) = \frac{q_i q_j e^2}{r_{ij}} + A_{ij} \exp(-B_{ij} r_{ij}) - \frac{C_{ij}}{r_{ij}^6} . \quad (1)$$

The values of the partial charges q_i and the constants A_{ij} , B_{ij} can be found in Ref. [4]. Since the quantity we want to investigate, $c(\nu)$, is a collective one, it is necessary to average it over many independent realizations. Thus the system sizes we used are rather small, 336 ions, despite the fact that the dynamics of such a small system will show appreciable finite size effects [5]. However, exploratory runs with larger systems showed that these effects do not change the results substantially. The simulations were done at constant volume using a box size of 16.8 Å, thus at a density of 2.36g/cm³, close to the experimental value of the density, which is at 2.2g/cm³. The equations of motion have been integrated with the velocity form of the Verlet algorithm with a time step of 1.6 fs. The temperatures investigated were 6100 K, 4700 K, 4000 K, 3580 K, 3250 K, and 3000 K. At all temperatures the system was first equilibrated for a time which is significantly longer than the typical α -relaxation time of the system at this temperature.

RESULTS

In real experiments the frequency dependent specific heat is usually measured in the *NPT* ensemble. Although algorithms exist with which the *static equilibrium* properties of a system can be measured in a simulation in this ensemble, these algorithms introduce an artificial dynamics of the particles and are therefore not suited to investigate the dynamical properties of the system in this ensemble. Hence we calculated the frequency dependent specific heat in the microcanonical ensemble. Whereas in the *NPT* ensemble the specific heat is related to the fluctuations of the enthalpy, in the *NEV* ensemble it is related to the fluctuations of the kinetic energy [2,6]. It can be shown that in this ensemble the specific heat at frequency ν is given by

$$c(\nu) = \frac{k_B}{2/3 - K(t=0) - i2\pi\nu \int_0^\infty dt \exp(i2\pi\nu t) K(t)} , \quad (2)$$

where $K(t)$ is the autocorrelation function of the kinetic energy E_{kin} and is defined as

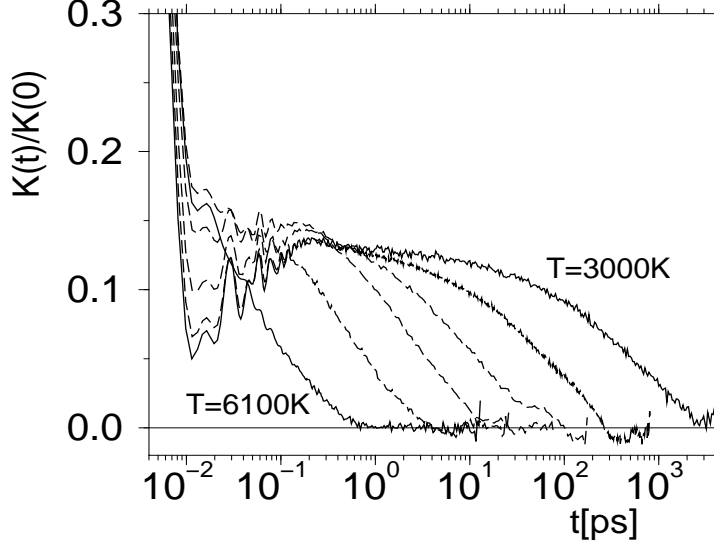


FIGURE 1. Time dependence of the autocorrelation function of the kinetic energy for all temperatures investigated.

$$K(t) = \frac{N}{\bar{E}_{\text{kin}}^2} \left[(E_{\text{kin}}(t) - \bar{E}_{\text{kin}})(E_{\text{kin}}(0) - \bar{E}_{\text{kin}}) \right] \quad . \quad (3)$$

Here \bar{E}_{kin} is the mean kinetic energy and N is the total number of ions. The derivation of Eq. (2) can be found in Ref. [6].

From Eq. (2) we see that the relevant quantity is the autocorrelation function $K(t)$. The time dependence of this quantity, normalized by its value at time $t = 0$, is shown in Fig. 1 for all the temperatures we investigated.

From this figure we recognize that for high temperatures $K(t)/K(0)$ decays very quickly to a value around 0.13 and then goes to zero like a stretched exponential. With decreasing temperature the function shows a plateau at intermediate times, the length of which increases quickly with decreasing temperature. Such a time and temperature dependence is very similar to the one found for the relaxation behavior of structural quantities, such as the intermediate scattering function [7]. Apart from these features the curves for the lowest temperatures show also a local minimum at around 0.02 ps, the depth of which increases with decreasing temperatures. The existence of this dip, as well as the observed high frequency oscillations, can be understood by realizing that within the harmonic approximation, which will be valid at even lower temperatures, the correlator is closely related to the autocorrelation function of the velocity, which is well known to show such a dip.

Using Eq. (2) we calculated from $K(t)$ the frequency dependent specific heat $c(\nu)$. The real and imaginary part of this quantity are shown in Fig. 2 for all temperatures investigated. Let us first discuss $c'(\nu)$: For very high frequencies we expect this function to go to the ideal gas value of 1.5, since the configurational degrees of freedom are not able to take up energy at such high frequencies. With decreasing ν the function shows a fast increase in the frequency range which corresponds

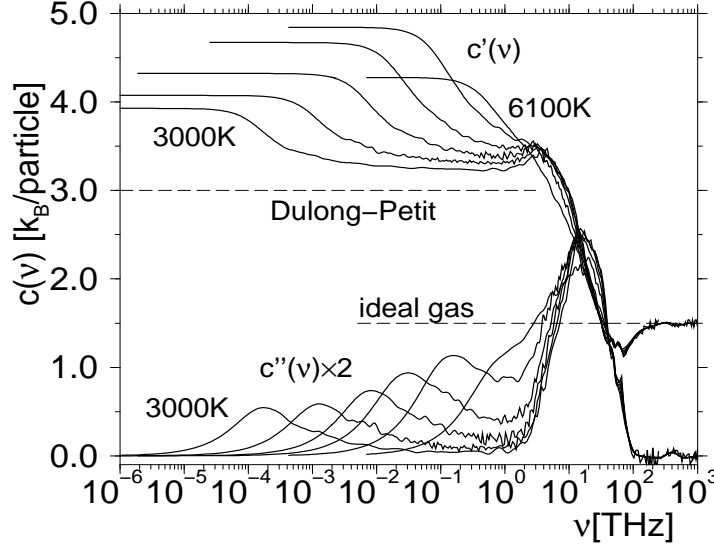


FIGURE 2. Frequency dependence of the real and imaginary part (times 2.0) of the specific heat for all temperatures investigated. The upper and lower dashed lines are the values of $c'(\nu)$ for the harmonic solid and the ideal gas, respectively.

to the microscopic vibrations. For low temperatures this regime is followed by a plateau the height of which corresponds to the static specific heat of the system *if no relaxation would take place*, i.e. to the specific heat of the vibrational degrees of freedom. Since, however, on the time scale of the α -relaxation time the system relaxes, $c'(\nu)$ shows at the corresponding frequencies a further upward step. This feature is related to the fact that for very long times, or small frequencies, those configurational degrees of freedom which are not of vibrational type are relaxing and thus can take up energy. At even smaller frequencies the curves then show a plateau, the height of which is the static specific heat of the system. We see that with decreasing temperature this value is decreasing but is always significantly above the harmonic value given by the Dulong-Petit value of 3.0, since the relaxing configurational degrees of freedom give rise to an enhancement of the static specific heat.

We also note that the height of the first step in $c'(\nu)$ [coming from the low frequency side] is the configurational part of the specific heat. We see that at the lowest temperature this height is rather small, $0.7k_B$ per particle, in agreement with the experimental observation for strong glass-formers.

All these features can also be seen well in the imaginary part of $c(\nu)$. At high frequencies we have a microscopic peak which corresponds to the vibrational degrees of freedom. The location and the height of this peak is essentially independent of temperature. At intermediate and low temperatures a second peak is seen at low frequencies, the so-called α -peak. Its position depends strongly on temperature in agreement with the observation that the α -relaxation time of structural quantities increases quickly with decreasing temperatures [7]. From the location of this peak

we can read off ν_{\max} , the frequency scale of the relaxation of the specific heat. As it will be shown elsewhere [6], the product of ν_{\max} with $\tau(T)$, the α -relaxation time of the intermediate scattering function, is essentially independent of the temperature, thus showing the intimate connection between the frequency dependent specific heat and the structural relaxation, in agreement with the prediction of Götze and Latz [8].

To summarize we can say that we have presented the results of a large scale molecular dynamics computer simulation of a realistic model of viscous silica to investigate the frequency dependence of the specific heat. In the frequency regime which is accessible also to experiments our results are in qualitative agreement with the experimental data [3]. At higher frequencies we see the influence of the vibrational degrees of freedom on $c(\nu)$. Since no experimental data for $c(\nu)$ is available for silica we are not able to compare the results of the present simulations with reality. However, in a previous investigation we have shown that the present model gives very good quantitative agreement of the *static* specific heat with the one of real silica [9] and thus it is not unreasonable to assume that the results of the simulation on the dynamic quantity is reliable also.

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